

WHAT IS CLAIMED IS:

1. A mass analysis apparatus comprising a first ion source which ionizes a sample and produces sample ions, a second ion source which produces ions having a polarity opposite to the polarity of the sample ions, and a mass spectrometer, wherein said second ion source is provided between said first ion source and said mass spectrometer apart from the axis of a flow of the sample ions discharged from said first ion source and emits ions to the flow of sample ions discharged from said first ion source.

2. The mass analysis apparatus of claim 1, wherein said first and second ion sources are atmospheric pressure ion sources that perform ionization at the atmospheric pressure and ions emitted from said first and second ion sources cross also at the atmospheric pressure.

3. The mass analysis apparatus of claim 1, wherein said first ion source is selected from a group of electro spray (ESI), pneumatically assisted electro spray, nano-spray, sonic spray (SSI), and MALDI ion sources.

4. The mass analysis apparatus of claim 2, wherein said second ion source is an atmospheric pressure chemical ionization ion source.

5. The mass analysis apparatus of claim 4, wherein  
said second ion source comprises a corona discharge  
electrode, a shield electrode which is formed to cover  
said corona discharge electrode and has an opening to  
5 emit the generated ions, and a power source to supply  
a voltage to said corona discharge electrode.

6. The mass analysis apparatus of claim 5, wherein  
said shield electrode is made of a conductive metal  
material and said opening is covered with a metal mesh.

10 7. The mass analysis apparatus of claim 5, wherein  
said shield electrode is kept at the ground potential.

8. The mass analysis apparatus of claim 1, wherein  
said second ion source is equipped with an inlet  
section which introduces a compound for accelerating  
15 generation of ions.

9. The mass analysis apparatus of claim 8, wherein  
said compound is selected from a group of alcohols and  
non-ionic surfactant.

10. The mass analysis apparatus of claim 1,  
20 wherein said second ion source is provided between  
said first ion source and said mass spectrometer.

11. A mass analysis apparatus comprising a first  
atmospheric pressure ion source which ionizes a sample  
and produces sample ions, a shield electrode made of a  
25 cylindrical metal mesh, a corona discharge electrode

provided outside said shield electrode, a second atmospheric pressure ion source equipped with a power supply which supplies a voltage to said corona discharge electrode to generate ions having a polarity opposite to that of the sample ions, and a mass spectrometer, wherein the sample ions emitted from said first atmospheric pressure ion source are introduced into said shield electrode along the central axis of said shield electrode and made to react with ions generated by said second atmospheric pressure ion source, and ions passing through said shield electrode are introduced into said mass spectrometer for mass spectroscopy.

12. The mass analysis apparatus of claim 11, wherein said shield electrode is kept at a ground potential.

13. The mass analysis apparatus of claim 11, wherein said corona discharge electrode is a needle electrode and a plurality of corona discharge electrodes are provided outside said shield electrode.

14. The mass analysis apparatus of claim 11, wherein said corona discharge electrodes are disposed around said shield electrode apart therefrom in a ring form.

15. The mass analysis apparatus of claim 14,

wherein said corona discharge electrodes are made of thin metal wires.

16. The mass analysis apparatus of claim 14,  
wherein said corona discharge electrode is made of a  
5 ring-shaped metal plate electrode.

17. The mass analysis apparatus of claim 11,  
wherein said corona discharge electrode is a  
cylindrical metal mesh placed around said shield  
electrode apart therefrom.

10 18. A mass spectrometer comprising a first  
atmospheric pressure ion source which ionizes a sample  
and produces sample ions, a cylindrical metal mesh, a  
shield electrode made of a plurality of metallic  
dividing walls on the outer periphery of said metal  
15 mesh, a plurality of corona discharge electrode  
provided in a ring manner between said dividing walls  
outside said shield electrode, and a second  
atmospheric pressure ion source equipped with a power  
supply which supplies a voltage to said corona  
20 discharge electrode to generate ions having a polarity  
opposite to that of the sample ions, and a mass  
spectrometer, wherein the sample ions emitted from  
said first atmospheric pressure ion source are  
introduced into said shield electrode along the  
25 central axis of said shield electrode and made to

react with ions generated by said second atmospheric pressure ion source, and ions passing through said shield electrode are introduced into said mass spectrometer for mass spectroscopy.

5           19. The mass analysis apparatus of claim 18, wherein said corona discharge electrodes are thin metallic wires.

          20. The mass analysis apparatus of claim 18, wherein said corona discharge electrode is made of a  
10   ring-shaped metal plate electrode.

          21. The mass analysis apparatus of claim 18, wherein said power supply is provided for each corona discharge electrode.

          22. The mass analysis apparatus of claim 18,  
15   wherein said first and second ion sources and said mass spectrometer are disposed so that the axis along which said first atmospheric pressure ion source emits sample ions through said second atmospheric pressure ion source may intersect the axis along which ions are  
20   introduced into small aperture of said mass spectrometer.

          23. A mass spectrometry by a mass spectrometer comprising a first ion source which ionizes a sample and produces sample ions, a second ion source which  
25   generates reactant ions having a polarity opposite to

that of the sample ions and emits the reactant ions to  
said sample ions, and a mass spectrometer which  
receives a mixture of said reactant ions and the  
sample ions and performs a mass spectroscopy thereon,  
5 wherein said mass spectrometric method comprises the  
steps of generating reactant ions by said second ion  
source intermittently and periodically while said  
first ion source generates sample ions continuously,  
mass-scanning said mass spectrometer respectively  
10 while said second ion source makes ionization and while  
said second ion source does not make ionization, and  
obtaining mass spectra thereof.

24. A mass spectrometry by a mass spectrometer  
comprising a first ion source which ionizes a sample  
15 and produces sample ions, a second ion source which  
generates reactant ions having a polarity opposite to  
that of the sample ions and emits the reactant ions to  
said sample ions, and a mass spectrometer which  
receives a mixture of said reactant ions and the  
20 sample ions and performs a mass spectroscopy thereon,  
wherein said mass spectrometric method comprises the  
steps of generating reactant ions by said second ion  
source intermittently and periodically while said  
first ion source generates sample ions continuously,  
25 mass-scanning said mass spectrometer several times

respectively while said second ion source makes ionization and while said second ion source does not make ionization, and obtaining mass spectra thereof.

25. A mass spectrometry by a mass spectrometer  
5 comprising a first ion source which ionizes a sample and produces sample ions, a second ion source which comprises a corona discharge electrode and a power supply for applying a voltage to said electrode, generates reactant ions having a polarity opposite to  
10 that of the sample ions and emits the reactant ions to said sample ions, and a mass spectrometer which receives a mixture of said reactant ions and the sample ions and performs a mass spectroscopy thereon,  
wherein said mass spectrometric method comprises a  
15 step of step-by-step varying the voltage which is applied from said power supply of said second ion source to said corona discharge electrode while said first ion source ionizes continuously.

26. A mass spectrometry by a mass spectrometer  
20 comprising a first ion source which ionizes a sample and produces sample ions, a second ion source which comprises a plurality of corona discharge electrodes and power supplies for applying a voltage to said electrodes, generates reactant ions having a polarity  
25 opposite to that of the sample ions and emits the

reactant ions to said sample ions, and a mass spectrometer which receives a mixture of said reactant ions and the sample ions and performs a mass spectroscopy thereon, wherein said mass spectrometric  
5 method comprises a step of shifting voltage applying periods of corona discharge electrodes of said second ion source respectively while said first ion source ionizes continuously.

27. A mass spectrometry by a mass spectrometer  
10 comprising a first ion source which ionizes a sample and produces sample ions, a second ion source which comprises corona discharge electrodes and power supplies for applying a voltage to said electrodes, generates reactant ions having a polarity opposite to  
15 that of the sample ions and emits the reactant ions to said sample ions, and a mass spectrometer which receives a mixture of said reactant ions and the sample ions and performs a mass spectroscopy thereon, wherein said mass spectrometric method comprises a  
20 first step of controlling said power supplies to zero the discharge current to said corona discharge electrode and collecting mass spectra, a second step of totaling all ion intensities in a preset mass range, computing a corona discharge current value or applied  
25 voltage from the total ion intensity, setting the



corona discharge current value or applied voltage to said power supply, and collecting mass spectra, and said first and second steps are repeated periodically.